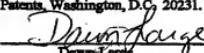


FORM PTO-1298 (REV. 0-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				3017.001 Wray
INTERNATIONAL APPLICATION NO. PCT/AU00/00719	INTERNATIONAL FILING DATE 23 June 2000			U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 10/019474
TITLE OF INVENTION NATURAL GAS HYDRATE AND METHOD FOR PRODUCING SAME				PRIORITY DATE CLAIMED 24 June 1999
APPLICANT(S) FOR DO/EO/US Alan Terence Jackson & Robert Amin				
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:				
<p>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input type="checkbox"/> This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).</p> <p>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).</p> <p>5. <input type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). courtesy copy b. <input type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <p>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p>				
Items 11 to 16 below concern document(s) or information included:				
<p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</p> <p>14. <input type="checkbox"/> A substitute specification.</p> <p>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>16. <input type="checkbox"/> Other items or information:</p>				
Certificates of Mailing by "Express Mail"				
Express Mail Mailing Number <u>EL860833935</u> Date of Deposit <u>December 21, 2001</u> I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents, Washington, D.C. 20231.  <u>Dawn Lengle</u>				

10/01/97		INTERNATIONAL APPLICATION NO. PCT/AU00/00719	ATTORNEY'S DOCKET NUMBER 3017-001 Wray																																		
<p>17. <input checked="" type="checkbox"/> The following fees are submitted:</p> <p>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5) :</p> <table> <tr> <td>Neither international preliminary examination fee (37 CFR 1.482)</td> <td>\$ 1,040</td> </tr> <tr> <td>nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO</td> <td>\$1,040.00</td> </tr> <tr> <td>and International Search Report not prepared by the EPO or JPO</td> <td></td> </tr> <tr> <td>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO.....</td> <td>\$860.00</td> </tr> <tr> <td>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO</td> <td>\$710.00</td> </tr> <tr> <td>International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4).....</td> <td>\$690.00</td> </tr> <tr> <td>International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)</td> <td>\$100.00</td> </tr> </table> <p align="center">ENTER APPROPRIATE BASIC FEE AMOUNT = \$1,040.00</p> <p>Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).</p> <table> <thead> <tr> <th>CLAIMS</th> <th>NUMBER FILED</th> <th>NUMBER EXTRA</th> <th>RATE</th> </tr> </thead> <tbody> <tr> <td>Total claims</td> <td>41</td> <td>- 20 = 21</td> <td>X \$18.00 \$ 378.00</td> </tr> <tr> <td>Independent claims</td> <td>2</td> <td>- 3 = 0</td> <td>X \$80.00 \$ -0-</td> </tr> <tr> <td>MULTIPLE DEPENDENT CLAIM(S) (if applicable)</td> <td></td> <td></td> <td>+ \$270.00 \$ -0-</td> </tr> </tbody> </table> <p align="center">TOTAL OF ABOVE CALCULATIONS = \$ 1,548.00</p> <p><input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.</p> <p align="right">SUBTOTAL = \$ 1,548.00</p> <p>Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).</p> <p align="right">TOTAL NATIONAL FEE = \$ 1,548.00</p> <p>Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property</p> <p align="right">TOTAL FEES ENCLOSED = \$ 1,548.00</p> <table> <tr> <td>Amount to be refunded:</td> <td>\$</td> </tr> <tr> <td>charged:</td> <td>\$</td> </tr> </table>				Neither international preliminary examination fee (37 CFR 1.482)	\$ 1,040	nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO	\$1,040.00	and International Search Report not prepared by the EPO or JPO		International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO.....	\$860.00	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	\$710.00	International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4).....	\$690.00	International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)	\$100.00	CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	Total claims	41	- 20 = 21	X \$18.00 \$ 378.00	Independent claims	2	- 3 = 0	X \$80.00 \$ -0-	MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00 \$ -0-	Amount to be refunded:	\$	charged:	\$
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<p>a. <input checked="" type="checkbox"/> A check in the amount of \$ 1,548.00 to cover the above fees is enclosed.</p> <p>b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 50-0852. A duplicate copy of this sheet is enclosed.</p>																																					
<p>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p> <p>SEND ALL CORRESPONDENCE TO: Steven L. Permut REISING, ETHERINGTON, BARNES, KISSELLE, LEARMAN & McCULLOCH, P.C. P.O. Box 4390 Troy, Michigan 48099-4390 (248) 689-3500</p> <p></p> <p>SIGNATURE: Steven L. Permut NAME 28,388 REGISTRATION NUMBER</p>																																					

10/019474

531 Rec'd PCT/PCT 21 DEC 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No.: 3017.001 Wray

In re application:

Alan Terence Jackson & Robert Amin

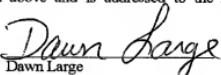
Filed: Herewith

National Filing for: PCT/AU00/00719

For: NATURAL GAS HYDRATE AND METHOD FOR PRODUCING

CERTIFICATE OF MAILING BY "EXPRESS MAIL"

"EXPRESS MAIL" Mailing Label No. EL860833935US Date of Deposit, December 21, 2001 hereby certify That this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner For Patents, Washington, DC 20231.


Dawn Large

PRELIMINARY AMENDMENT

Assistant Commissioner For Trademarks
Washington, DC 20231

Dear Sir:

Please amend the above-identified patent application as follows:

IN THE CLAIMS:

Delete claims 5 - 10 and 12-43 and substitute new claims 44 -79 therein.

IN THE ABSTRACT:

Please insert the attached new abstract.

Please charge any additional fees or credit any overpayment to our Deposit Account No. 18-0853, a duplicate of this sheet is attached.

Respectfully submitted,

REISING, ETHINGTON, BARNES, KISSELLE,
LEARMAN & McCULLOCH, PC


Steven L. Permut
Reg. No. 28,388
P.O. Box 4390
Troy, Michigan 48099
(248) 689-3500

Date: December 21, 2001

New Claims:

44. A natural gas hydrate according to claim 1 characterised by a hydrate desolution temperature in excess of -15°C at atmospheric pressure.

45. A natural gas hydrate according to claim 1 characterised by a hydrate desolution temperature in excess of -13°C at atmospheric pressure.

46. A natural gas hydrate according to claim 1 characterised by a hydrate desolution temperature in excess of -11°C at atmospheric pressure.

47. A natural gas hydrate according to claim 1 characterised by a hydrate desolution temperature in excess of -5°C at atmospheric pressure.

48. A natural gas hydrate according to claim 1 characterised by a hydrate desolution temperature in excess of -3°C at atmospheric pressure.

49. A natural gas hydrate according to claim 1 characterised by a hydrate desolution temperature in excess of 3°C at atmospheric pressure.

50. A natural gas hydrate according to claim 11 characterised by a hydrate desolution temperature in excess of approximately 0°C at approximately atmospheric pressure.

51. A natural gas hydrate according to claim 11 characterised by a hydrate desolution temperature in excess of approximately 1°C at approximately atmospheric pressure.

52. A natural gas hydrate according to claim 11 characterised by a hydrate desolution temperature in excess of approximately 2°C at approximately atmospheric pressure.

53. A natural gas hydrate according to claim 11 characterised by a hydrate desolution temperature in excess of approximately 3°C at approximately atmospheric pressure.

54. A natural gas hydrate according to claim 11 characterised by a gas content in excess of 180 Sm³ per m³.

55. A natural gas hydrate according to claim 11 characterised by a gas content in excess of 186 Sm³ per m³.

56. A natural gas hydrate according to claim 11 characterised by a gas content in excess of 220 Sm³ per m³.

57. A natural gas hydrate according to claim 11 characterised by a gas content in excess of 227 Sm³ per m³.

58. A method for the production of the natural gas hydrate of claim 1 characterised by the steps of:-

combining natural gas and water to form a natural-gas water system and an agent adapted to reduce the natural gas-water interfacial tension to form a natural-gas water-agent system;

allowing the natural gas-water-agent system to reach equilibrium at elevated pressure and ambient temperature; and

reducing the temperature of the natural gas-water-agent system to initiate the formation of the natural gas hydrate.

59. A method of according to claim 58 characterised by the additional step of, before combining the natural gas and water, atomising the natural gas and water.

60. A method according to claim 58 characterised by the natural gas-water-agent system being agitated before the temperature is reduced.

61. A method according to claim 58 characterised in that the agent is a compound that is at least partially soluble in water.

62. A method according to claim 61 characterised in that the agent is an alkali metal alkylsulfonate.

63. A method according to claim 61 characterised in that the agent is a sodium alkylsulfonate.

64. A method according to claim 61 characterised in that the agent is selected from the group; sodium lauryl sulfate, sodium 1-propanesulfonate, sodium 1-butane sulfonate, sodium 1-pentanesulfonate, sodium 1-hexane sulfonate sodium 1-heptane sulfonate, sodium 1-octanesulfonate, sodium 1-nonanesulfonate, sodium 1-decanesulfonate, sodium 1-undecanesulfonate, sodium 1-dodecanesulfonate and sodium 1-tridecane sulfonate.

65. A method according to claim 61 characterised in that the amount of agent added is such that the concentration of the agent in the natural gas-water-agent system is less than about 1% by weight.

66. A method according to claim 61 characterised in that the amount of agent added results in a concentration of the agent less than about 0.5% by weight.

67. A method according to claim 61 characterised in that the amount of agent added results in a concentration of the agent between about 0.1 and 0.2% by weight.

68. A method according to claim 61 characterised in that the agent is sodium lauryl sulfate.

69. A method according to claim 61 characterised in that the agent is sodium lauryl sulfate and the amount of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is less than about 1% by weight.

70. A method according to claim 61 characterised in that the agent is sodium lauryl sulfate and the amount of agent added results in a concentration of the agent less than about 0.5% by weight.

71. A method according to claim 61 characterised in that the agent is sodium lauryl sulfate and the amount of agent added results in a concentration of the agent between about 0.1 and 0.2% by weight.

72. A method according to claim 61 characterised in that the agent is sodium tripolyphosphate.

73. A method according to claim 61 characterised in that the agent is sodium tripolyphosphate and the amount of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is between about 1 and 3 % by weight.

74. A method according to claim 61 characterised in that the agent is an alcohol.

75. A method according to claim 61 characterised in that the agent is isopropyl alcohol.

76. A method according to either claim 61 characterised in that the agent is isopropyl alcohol and the amount of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is about 0.1 % by volume.

77. A method according to claim 58 characterised in that the pressure exceeds about 50 bars.

78. A method according to claim 58 characterised in that the temperature is below about 18°C.

79. A method according to claim 58 wherein the natural-gas-water-agent system is constantly mixed throughout the method.

ABSTRACT

A method for the production of the natural gas hydrate characterised by the steps of: combining natural gas and water to form a natural-gas water system and an agent adapted to reduce the natural gas-water interfacial tension to form a
5 natural-gas water-agent system, allowing the natural gas-water-agent system to reach equilibrium at elevated pressure and ambient temperature and reducing the temperature of the natural gas-water-agent system to initiate the formation of the natural gas hydrate.

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10/019474

Natural Gas Hydrate And Method For Producing Same**Field Of The Invention**

The present invention relates to a natural gas hydrate. More particularly, the present invention relates to a natural gas hydrate with improved gas content and

5 stability characteristics and a method for producing the same.

Background Art

Natural gas hydrates are a stable solid comprising water and natural gas, and have been known to scientists for some years as a curiosity. More recently,

natural gas hydrates became a serious concern in regard to the transportation
10 and storage of natural gas industries in cold climates, due to the tendency of hydrates to form in pipelines thereby blocking the flow the pipelines.

Natural gas hydrates may be formed by the combination of water and gas at relatively moderate temperatures and pressures, with the resulting solid having the outward characteristics of ice, being either white or grey in colour and cold to

15 the touch. At ambient temperatures and pressures natural gas hydrates break down releasing natural gas.

Conventionally, gas storage is achieved through re-injecting into reservoirs, or pressurised reservoirs or through the use of line pack, where the volume of the pipeline system is of the same order of magnitude as several days' customer

20 consumption. The use of natural gas hydrates in storage has the potential to provide a flexible way of storing reserves of natural gas to meet short to medium term requirements in the event of excessive demands or a reduction in the delivery of gas from source.

In any application, the gas content of the hydrate and the temperature at which

25 the hydrate begins to decompose (i.e. the hydrate desolution temperature), are significant criteria that require consideration. Known natural gas hydrates exhibit

a gas content of 163 Sm³ per m³ of hydrate, and a hydrate desolution temperature, at atmospheric pressure, of -15°C.

It is one object of the present invention to provide a natural gas hydrate and a method for the production thereof, with improved gas content and hydrate desolution temperature.

Throughout the specification, unless the context requires otherwise, the word "comprise" or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

10 Disclosure Of The Invention

In accordance with the present invention there is provided a natural gas hydrate with a gas content in excess of 163 Sm³ per m³. Preferably, the natural gas hydrate has a gas content in excess of 170 Sm³ per m³. Preferably still, the natural gas hydrate has a gas content in excess of 180 Sm³ per m³. Further and

15 still preferably, the natural gas hydrate has a gas content of 186 Sm³ per m³. In a highly preferred form of the invention, the natural gas hydrate has a gas content in excess of 220 Sm³ per m³. Preferably still, the natural gas hydrate has a gas content in excess of approximately 227 Sm³ per m³.

Preferably, the natural gas hydrate exhibits a hydrate desolution temperature in
20 excess of -15°C at atmospheric pressure. Preferably still, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -13°C at atmospheric pressure. Further and still preferably, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -11°C at atmospheric pressure. In a highly preferred form of the invention, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -5°C at atmospheric pressure. Preferably still, the natural gas hydrate exhibits a hydrate desolution temperature in excess of 3°C at atmospheric pressure.

In accordance with the present invention, there is further provided a natural gas hydrate which exhibits a hydrate desolution temperature in excess of -15°C at atmospheric pressure. Preferably, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -13°C at atmospheric pressure. Preferably still, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -11°C at atmospheric pressure. Further and still preferably, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -5°C at atmospheric pressure. In a highly preferred form of the invention, the natural gas hydrate exhibits a hydrate desolution temperature in excess of 3°C at atmospheric pressure.

Preferably, the natural gas hydrate has a gas content in excess of 163 Sm³ per m³. Preferably still, the natural gas hydrate has a gas content in excess of 170 Sm³ per m³. Further and still preferably, the natural gas hydrate has a gas content in excess of 180 Sm³ per m³. In a highly preferred form of the invention, the natural gas hydrate has a gas content of 186 Sm³ per m³. In one form of the invention, the natural gas hydrate has a gas content in excess of 220 Sm³ per m³. Preferably still, the natural gas hydrate has a gas content in excess of approximately 227 Sm³ per m³.

In accordance with the present invention there is still further provided a method for the production of the natural gas hydrate of the present invention, the method comprising the steps of:-

combining natural gas and water to form a natural-gas water system and an agent adapted to reduce the natural gas-water interfacial tension to form a natural-gas water-agent system;

allowing the natural gas-water-agent system to reach equilibrium at elevated pressure and ambient temperature; and

reducing the temperature of the natural gas-water-agent system to initiate the formation of the natural gas hydrate.

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Preferably, the method of the present invention comprises the additional step of, before combining the natural gas and water, atomising the natural gas and water.

Preferably, the natural gas-water-agent system is agitated before the temperature is reduced.

5 Preferably, the agent is a compound that is at least partially soluble in water.

In one form of the invention, the agent is an alkali metal alkylsulfonate. Preferably, where the agent is an alkali metal alkylsulfonate, the alkali metal alkylsulfonate is a sodium alkylsulfonate. Where the agent is a sodium alkylsulfonate, the agent may be selected from the group; sodium lauryl sulfate,

10 sodium 1-propanesulfonate, sodium 1-butane sulfonate, sodium 1-pentanesulfonate, sodium 1-hexane sulfonate sodium 1-heptane sulfonate, sodium 1-octanesulfonate, sodium 1-nananesulfonate, sodium 1-decanesulfonate, sodium 1-undecanesulfonate, sodium 1-dodecanesulfonate and sodium 1-tridecane sulfonate.

15 Where the agent is an alkali metal sulfonate, the amount of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is less than about 1% by weight. Preferably still, the amount of agent added results in a concentration of the agent less than about 0.5% by weight. Further and still preferably, the amount of agent added results in a concentration of the agent between about 0.1 and 0.2% by weight.

20 In an alternate form of the invention, the agent is sodium lauryl sulfate. Where the agent is sodium lauryl sulfate, the amount of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is less than about 1% by weight. Preferably still, the amount of agent added results in a concentration of the agent less than about 0.5% by weight. Further and still preferably, the amount of agent added results in a concentration of the agent between about 0.1 and 0.2% by weight.

- 5 -

In an alternate form of the invention, the agent is sodium tripolyphosphate. Where the agent is sodium tripolyphosphate, the amount of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is between about 1 and 3 % by weight.

- 5 In an alternate form of the invention, the agent is an alcohol. Preferably, where the agent is an alcohol, the agent is isopropyl alcohol. Where the agent is isopropyl alcohol, the amount of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is about 0.1 % by volume.
- 10 The degree to which the temperature is decreased depends upon the degree to which the pressure is elevated. However, preferably the pressure exceeds about 50 bars and preferably, the temperature is below about 18°C.

Preferably, the natural-gas-water-agent system is constantly mixed throughout the hydration process.

15 Examples

The present invention will now be described in relation to five examples. However, it must be appreciated that the following description of those examples is not to limit the generality of the above description of the invention.

Hydrate Formation

20 Example 1 – isopropyl alcohol

Water and isopropyl alcohol (0.1% by volume) were introduced into a sapphire cell. The cell was pressurised with methane gas above the hydrate equilibrium pressure for a normal water-methane system. Equilibrium was achieved quickly by bubbling the methane through the water phase. The system was stabilised at 25 a pressure of 206 bars (3000psia) and room temperature of 23°C.

- 6 -

The temperature was then reduced at a rate of 0.1°C per minute using a thermostat air bath to 17.7°C. Crystals of methane hydrate were observed on the sapphire window, and hydrate formation was assumed to be complete when pressure had stabilised in the cell.

5 Example 2 – isopropyl alcohol

Water and isopropyl alcohol (0.1% by volume) were introduced into a sapphire cell. The cell was pressurised with methane gas above the hydrate equilibrium pressure for a normal water-methane system. Equilibrium was achieved quickly by bubbling the methane through the water phase. The system was stabilised at 10 a pressure of 138 bars (2000psia) and room temperature of 23°C.

The temperature was then reduced at a rate of 0.1°C per minute using a thermostat air bath to 15.5°C. Crystals of methane hydrate were observed on the sapphire window, and hydrate formation was assumed to be complete when pressure had stabilised in the cell.

15 Example 3 – isopropyl alcohol

Water and isopropyl alcohol (0.1% by volume) were introduced into a sapphire cell. The cell was pressurised with methane gas above the hydrate equilibrium pressure for a normal water-methane system. Equilibrium was achieved quickly by bubbling the methane through the water phase. The system was stabilised at 20 a pressure of 102 bars and room temperature of 23°C.

The temperature was then reduced at a rate of 0.1°C per minute using a thermostat air bath to 13.1°C. Crystals of methane hydrate were observed on the sapphire window, and hydrate formation was assumed to be complete when pressure had stabilised in the cell.

Example 4 – isopropyl alcohol

Water and isopropyl alcohol (0.1% by volume) were introduced into a sapphire cell. The cell was pressurised with methane gas above the hydrate equilibrium pressure for a normal water-methane system. Equilibrium was achieved quickly

5 by bubbling the methane through the water phase. The system was stabilised at a pressure of 54.5 bars (800psia) and room temperature of 23°C.

The temperature was then reduced at a rate of 0.1°C per minute using a thermostat air bath to 8.1°C. Crystals of methane hydrate were observed on the sapphire window, and hydrate formation was assumed to be complete when

10 pressure had stabilised in the cell.

Example 5 – sodium tripolyphosphate

Water and sodium tripolyphosphate (1% by weight) and methane gas were introduced into a sapphire cell. The pressure was adjusted to 1400 psia, and the mixture cooled rapidly to -5°C, where formation of the hydrate was observed. The

15 methane bubbling through the gas served to agitate the system.

Example 6 – sodium lauryl sulfate

Water and sodium lauryl sulfate (0.11% by weight) and methane gas were introduced into a sapphire cell. The mixture was pressurised to 2200psia at 30°C, and left to equilibrate for 45 minutes. The mixture was then flashed into a

20 cryogenic PVT cell at -3°C, causing the fluid to atomise and resulting in the formation of hydrate.

Example 7 – sodium 1-octanesulfonate

Water and sodium -octanesulfonate (0.15% by weight) and methane gas were introduced into a sapphire cell. The mixture was pressurised to 2200psia at 30°C,

25 and left to equilibrate for 45 minutes. The mixture was then flashed into a

- 8 -

cryogenic PVT cell at -3°C, causing the fluid to atomise and resulting in the formation of hydrate.

Example 8 – sodium 1-octanesulfonate

Water and sodium 1-octanesulfonate (0.1% by weight) and methane gas were 5 introduced into a sapphire cell. The mixture was pressurised to 2200psia at 30°C, and left to equilibrate for 45 minutes. The mixture was then flashed into a cryogenic PVT cell at -3°C, causing the fluid to atomise and resulting in the formation of hydrate.

Testing desolution temperature and natural gas content of hydrate

10 Example 1

Having formed the hydrate as outlined in Example 1, excess methane was removed and the temperature of the system was reduced to -15°C, at a rate of 0.1°C per minute, and the pressure of the system was observed to diminish to zero.

15 The hydrate was stored for more than 12 hours at -15°C, showing no observable changes in appearance. The pressure remained at zero throughout.

After 12 hours, the temperature of the system was gradually increased at a rate of 0.2°C per minute, in an attempt to reverse the hydrate formation process. Throughout this stage the pressure of the system was carefully monitored and 20 recorded by way of high precision digital pressure gauges. The pressure of the system remained stable until the temperature reached -11.5°C, at which point some increase was noted. The pressure continued to increase as the temperature increased until the pressure of the system stabilised at 206.3 bars at the ambient temperature of 23°C.

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Quantities of methane and water generated from the desolution of the hydrate were measured, and the methane content of the methane hydrate was calculated to be 186 Sm³ per m³.

Example 5

5 Having formed the hydrate as outlined in Example 5, the system was heated carefully. The hydrate was observed to melt at approximately 2°C. Based on the pressure-volume relationship, and excess methane before and after hydrate formation, the amount of methane contained in the hydrate was estimated to be in excess of 230 Sm³ per m³ of hydrate.

10 Examples 6 to 8

Having formed the hydrates as outlined in Examples 6 to 8, the systems were heated carefully. Each of the hydrates was observed to melt at approximately 3°C. Based on the pressure-volume relationship, and excess methane before and after hydrate formation, the amount of methane contained in the hydrate produced

15 in Example 6 was estimated to be in excess of 227 Sm³ per m³ of hydrate. Similarly, the amount of methane contained in the hydrate produced in Example 7 was estimated to be in excess of 212 Sm³ per m³ of hydrate. The amount of methane contained in the hydrate produced in Example 8 was estimated to be in excess of 209 Sm³ per m³ of hydrate.

20 Each unique mixture of hydrocarbon and water has its own hydrate formation curve, describing the temperatures and pressures at which the hydrate will form, and it is envisaged that additional analysis will reveal optimum pressure and temperature combinations, having regard to minimising the energy requirements for compression and cooling.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS

1. A natural gas hydrate characterised by a gas content in excess of 180 Sm³ per m³.
2. A natural gas hydrate according to claim 1 characterised by a gas content in excess of 186 Sm³ per m³.
5
3. A natural gas hydrate according to claim 1 characterised by a gas content in excess of 220 Sm³ per m³.
4. A natural gas hydrate according to claim 1 characterised by a gas content in excess of approximately 227 Sm³ per m³.
- 10 5. A natural gas hydrate according to any one of claims 1 to 6 characterised by a hydrate desolution temperature in excess of -15°C at atmospheric pressure.
6. A natural gas hydrate according to claim 7 characterised by a hydrate desolution temperature in excess of -13°C at atmospheric pressure.
15
7. A natural gas hydrate according to claim 7 characterised by a hydrate desolution temperature in excess of -11°C at atmospheric pressure.
8. A natural gas hydrate according to claim 7 characterised by a hydrate desolution temperature in excess of -5°C at atmospheric pressure.
20
9. A natural gas hydrate according to claim 7 characterised by a hydrate desolution temperature in excess of -3°C at atmospheric pressure.
10. A natural gas hydrate according to claim 7 characterised by a hydrate desolution temperature in excess of 3°C at atmospheric pressure.
25
11. A natural gas hydrate characterised by a hydrate desolution temperature in excess of approximately -1°C at approximately atmospheric pressure.

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12. A natural gas hydrate according to claim 1 characterised by a hydrate desolution temperature in excess of approximately 0°C at approximately atmospheric pressure.

13. A natural gas hydrate according to claim 12 characterised by a hydrate desolution temperature in excess of approximately 1°C at approximately atmospheric pressure.

14. A natural gas hydrate according to claim 13 characterised by a hydrate desolution temperature in excess of approximately 2°C at approximately atmospheric pressure.

10 15. A natural gas hydrate according to claim 14 characterised by a hydrate desolution temperature in excess of approximately 3°C at approximately atmospheric pressure.

16. A natural gas hydrate according to any one of claims 11 to 15 characterised by a gas content in excess of 180 Sm³ per m³.

15 17. A natural gas hydrate according to claim 16 characterised by a gas content in excess of 186 Sm³ per m³.

18. A natural gas hydrate according to claim 17 characterised by a gas content in excess of 220 Sm³ per m³.

19. A natural gas hydrate according to claim 16 characterised by a gas content in excess of 227 Sm³ per m³.

20. A method for the production of the natural gas hydrate of any one of claims 1 to 19 characterised by the steps of:-

25 combining natural gas and water to form a natural-gas water system and an agent adapted to reduce the natural gas-water interfacial tension to form a natural-gas water-agent system;

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allowing the natural gas-water-agent system to reach equilibrium at elevated pressure and ambient temperature; and

reducing the temperature of the natural gas-water-agent system to initiate the formation of the natural gas hydrate.

- 5 21. A method of according to claim 20 characterised by the additional step of, before combining the natural gas and water, atomising the natural gas and water.
22. A method according to claim 20 or claim 21 characterised by the natural gas-water-agent system being agitated before the temperature is reduced.
- 10 23. A method according to any one of claims 20 to 22 characterised in that the agent is a compound that is at least partially soluble in water.
24. A method according claim 23 characterised in that the agent is an alkali metal alkylsulfonate.
- 15 25. A method according to claim 24 characterised in that the alkali metal alkylsulfonate is a sodium alkylsulfonate.
26. A method according to claim 25 characterised in that the agent is selected from the group; sodium lauryl sulfate, sodium 1-propanesulfonate, sodium 1-butane sulfonate, sodium 1-pentanesulfonate, sodium 1-hexane sulfonate sodium 1-heptane sulfonate, sodium 1-octanesulfonate, sodium 1-nonanesulfonate, sodium 1-decanesulfonate, sodium 1-undecanesulfonate, sodium 1-dodecanesulfonate and sodium 1-tridecane sulfonate.
27. A method according to any one of claims 24 to 26 characterised in that the amount of agent added is such that the concentration of the agent in the natural gas-water-agent system is less than about 1% by weight.
- 25 28. A method according to claim 27 characterised in that the amount of agent added results in a concentration of the agent less than about 0.5% by weight.

29. A method according to claim 28 characterised in that the amount of agent added results in a concentration of the agent between about 0.1 and 0.2% by weight.

30. A method according to claim 23 characterised in that the agent is sodium lauryl sulfate.

31. A method according to claim 30 characterised in that the amount of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is less than about 1% by weight.

32. A method according to claim 31 characterised in that the amount of agent added results in a concentration of the agent less than about 0.5% by weight.

33. A method according to claim 32 characterised in that the amount of agent added results in a concentration of the agent between about 0.1 and 0.2% by weight.

34. A method according to claim 23 characterised in that the agent is sodium tripolyphosphate.

35. A method according to claim 34 characterised in that the amount of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is between about 1 and 3 % by weight.

36. A method according to claim 23 characterised in that the agent is an alcohol.

37. A method according to claim 36 characterised in that the agent is isopropyl alcohol.

38. A method according to either claim 36 or 37 characterised in that the amount of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is about 0.1 % by volume.

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39. A method according to any one of claims 20 to 38 characterised in that the pressure exceeds about 50 bars.
40. A method according to any one of claims 20 to 39 characterised in that the temperature is below about 18°C.
- 5 41. A method according to any one of the preceding claims wherein the natural-gas-water-agent system is constantly mixed throughout the method.
42. A method for the production of the natural gas hydrate substantially described herein with reference to any one of Examples 1 to 8.
43. A natural gas hydrate substantially as herein described.

10

AMENDED SHEET
IPEA/AU

PATENT

Attorney's Docket No. 0122.3017.001

COMBINED DECLARATION AND POWER OF ATTORNEY

(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL,
DIVISIONAL, CONTINUATION OR CIP)

As a below named inventor, I hereby declare that:

TYPE OF DECLARATION

This declaration is of the following type: (check one applicable item below)

- original
- design
- supplemental

NOTE: If the declaration is for an international Application being filed as a divisional, continuation or continuation-in-part application do not check next item; check appropriate one of last three items

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NOTE: If one of the follow 3 items apply then complete and also attach ADDED PAGES FOR
DIVISIONAL, CONTINUATION OR CIP

- divisional
- continuation
- continuation-in-part (CIP)

INVENTORSHIP IDENTIFICATION

WARNING: If the inventors are each not the inventors of all the claims an explanation of the facts, including the ownership of all the claims at the time the last claimed invention was made, should be submitted.

My residence, post office address and citizenship are as stated below next to my name, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

NATURAL GAS HYDRATE AND METHOD FOR PRODUCING

SPECIFICATION IDENTIFICATION

the specification of which: (complete (a), (b) or (c))

(a) is attached hereto.

(b) was filed on _____ as Serial No. _____ or _____
and was amended on _____ (if applicable). NOTE: Amendments filed after the original papers are deposited with the PTO which contain new matter are not accorded a filing date by being referred to in the declaration. Accordingly, the amendments involved are those filed with the application papers or, in the case of a supplemental declaration, are those amendments claiming matter not encompassed in the original statement of invention or claims. See 37 CFR 1.67.

(c) was described and claimed in PCT International Application No. PCT/AU00/00719 filed on 23 June 2000 and as amended under PCT Article 19 on _____ (if any).

205040-47167002

ACKNOWLEDGEMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56(a).

 In compliance with this duty there is attached an information disclosure statement 37 CFR 1.92.

PRIORITY CLAIM

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(complete (d) or (e))

(d) no such applications have been filed.

(e) X such applications have been filed as follows

NOTE: Where item (c) is entered above and the International Application which designated the U.S. claimed priority check item (e), enter the details below and make the priority claim.

**EARLIEST FOREIGN APPLICATION(S), IF ANY FILED WITHIN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION**

COUNTRY	APPLICATION NUMBER	DATE OF FILING (DAY, MONTH, YEAR)	PRIORITY CLAIM UNDER 35 USC 119
PCT	PCT/US00/00719	23 June 2000	<input checked="" type="checkbox"/> YES NO
Australia Provisional	PQ1188	24 June 1999	<input checked="" type="checkbox"/> YES NO
			YES NO
			YES NO
			YES NO

**ALL FOREIGN APPLICATION(S), IF ANY FILED MORE THAN 12 MONTHS
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POWER OF ATTORNEY

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.
(List name and registration number)

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DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code; and that such willful false statements may jeopardize the validity of the application of any patent issued thereon.

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